

Managing Paraffin Wax Deposition in Oil Well

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ABSTRACT

The presence of paraffin wax in crude oil has caused flow and mechanical problems while the oil is flowing from the wellbore via surface production tubing, facilities and trunkline to the crude oil terminal. Accurate knowledge of the potential for, and extent of, wax deposition can be critical in the successful design and operation of hydrocarbon production systems. Temperature is observed to be the main factor that controls the saturation of paraffin wax in oil. The decrease of temperature will result in the appearance of wax crystals. A simplified mathematical model was developed to predict the change of saturation of crude oil at subsequent temperature drops along the flow conduit. Paraffin wax crystallization occurs when the temperature of the oil drops below the wax appearance temperature. In this paper the authors present the causes and effects of such deposition and introduce predictive model to assist the prevention and mitigation measures through a case study.

Keywords

Organics Scale, Paraffin Wax and Asphaltene Deposition.

INTRODUCTION

Paraffin wax is a hydrocarbon component consists of mainly normal alkanes, varying amounts of condensed cycloalkanes, isoalkanes and occasionally a very low percentage of aromatic materials. Molecular weights are usually less than 450, and the viscosity at 210°F normally will be less than 6 cSt. Either needle or plate type crystal structures are common. The precipitation of wax from petroleum fluids may give rise to a variety of problems well known within the petroleum industry. The lighter components in crude oil keep the heavier components in solution. This solubility depends very strongly on the temperature. If the temperature of the oil is decreased, solubility of the heavy hydrocarbons may be sufficiently reduced to cause precipitation of these components in the form of solid wax crystals.

The presence of wax crystals changes the flow behavior of the crude oil from Newtonian to non-Newtonian. The wax crystals usually lead to higher viscosity with increased energy consumption for pumping and decreased capacity. In addition, if the oil is cooled during transportation, the wax crystals tend to deposit on the colder pipe wall. Wax deposits can lead to increased pipeline roughness, reduced effective diameter, more frequent pigging requirement and potential blockage. If these deposits get too thick, they can reduce the capacity of the pipeline and cause problems during pigging.

Holder and Winkler⁽¹⁾ studied the cloud and pour points for binary mixtures of n-paraffins ranging from C20 to C28. They concluded that binary mixtures of n-paraffins crystallize both independently and as solid solutions. As the difference in molecular weight between the two paraffins decreases, co-crystallization predominates. Bott and Gudmundsson⁽²⁾ studied the deposition of paraffin wax from kerosene in cooled heat-exchanger

tubes. They observed an asymptotic behaviour of wax deposition and attributed it to the decrease in heat flux and increase of shear stress. Burger (1981) investigated mechanisms of wax deposition in the Trans-Alaska Pipeline. It was found that only a small part of potentially precipitable hydrocarbons would deposit under favorable conditions.

CAUSES AND EFFECTS

Crystallization of solid paraffin is actually an example of liquid-solid phase equilibrium. It is explained in term of established principles of thermodynamics of solution. The solution of higher molecular weight hydrocarbons (HMWH) in lower molecular weight hydrocarbons that act as a solvent. Generally, high molecular weight solids precipitate whenever the carrying capacity of the fluid solvent decreases. Temperature was the main parameter that controls the fluid solvent saturation. Solubility of higher molecular weight hydrocarbons depends on temperature and the flow velocity in low pressure environment. In high-pressure situation such as in the production tubing, liberation of lighter hydrocarbons as gases due to pressure change reduces the solvent fraction of the reservoir fluid during transit from bottom hole to the surface. If larger pressure drops is allowed in the tubing liquid may contain large quantity of gases and the liquid flow rate decreased. HMWH may be exposed to longer heat loss and have greater tendency to crystallize and precipitate as wax.

MECHANISM OF LATERAL TRANSPORT OF WAXY RESIDUE

Migration of wax solids that formed from HMWH crystallization to the pipe wall is contributed by three lateral mechanisms, namely molecular diffusion,

Brownian diffusion, and shear dispersion. Gravity settling is also considered as a possible transport mechanism. Either one or more mechanisms are not present in flow or these effects are very weak, wax will remain in the flow streamline and no deposition occurred on the pipe wall.

Molecular Diffusion

For all flow conditions, oil will be in laminar flow either throughout the pipe or at least in a thin laminar sub-layer adjacent to the pipe wall. When oil is being cooled, there will be a temperature gradient across the laminar sub-layer. If temperatures are below that level where solid waxy crystals can be precipitated, then the flowing elements of oil will contain precipitated solid particles and the liquid phase will be in equilibrium with the solid phase. The temperature profile near the wall, therefore, will lead to a concentration gradient of dissolved wax, and this dissolved material will be transported toward the wall by molecular diffusion.

Brownian Diffusion

Small, solid waxy crystals, when suspended in oil, will be bombarded continually by thermally agitated oil molecules. These collisions will lead to small random Brownian movements of the suspended particles. If there is a concentration gradient of these particles, Brownian motion will lead to a net transport, which, in nature and mathematical description, is similar to diffusion.

Shear Dispersion

When small particles are suspended in a fluid that is in laminar motion, the particles transverse to the direction of local flow can arise, however, due to mutually induced velocity fields which occur during shear flow. The particle speed is that of the streamline at its center, and the particle rotates with an angular velocity, which is half the fluid shear rate. If the particle approaches a solid boundary, both linear and angular velocities will be reduced. Because of fluid viscosity, rotating particles will impart a circulatory motion to a layer of fluid adjacent to the particle. This rotating fluid region exerts a drag force on neighboring particles. In a shear field, each particle passes and interacts with nearby particles in slower or faster moving streamlines. If the particle concentration is high, then a significant number of multiparticle interactions will occur. These multiparticle collisions result in net lateral transport and a dispersing of particles.

Gravity Settling

Precipitated waxy crystals are denser than the surrounding liquid oil phase. Hence, if particles were non-interacting, they would settle in a gravity field and could be deposited on the bottom of pipes or tanks. Mathematical studies suggest that shear dispersion might redisperse settled solids in pipeline flow; therefore, any effect of gravity settling on wax deposition essentially would be eliminated.

OIL COMPOSITION ANALYSIS

The oil industry uses several standard test methods for identifying potential wax problems. The wax content is determined by UOP 46-64. This method is based on the precipitation of wax with acetone followed by filtration. Pour point is measured using the ASTM D-97-66 standard test method. Cloud point is determined using ASTM D-97-57; or a modification of this method is used to determine wax appearance or disappearance point.

Alternatively, a mathematical could also be used to calculate the wax precipitation temperature (cloud point) and the amount of wax potentially precipitated at any given temperature. However this model requires detail analytical information about oil composition or wax deposition as a function of temperature and thermal properties of oil. These data are needed for oil composition simulation and verification with measured data.

MATHEMATICAL MODEL

The thermodynamic behavior between gas and liquid phase which was presented by Won⁽⁴⁾ was used as a basis to the model. Won used regular solution theory to describe the non-idealities in the oil (liquid) and wax (solid) phases. The calculation was performed by imposing material and equilibrium K-value constraints. The overall material balance must be satisfied as shown in Equation 1. The material balance for each of the n-components in the feed must be satisfied.

The mole fraction in the feed is experimentally obtained from the oil composition analysis. The equilibrium K-values for each component in the feed describes the relationship between the wax mole fraction and the mole fraction of the oil. The activity coefficient for each component is estimated from the solubility parameter using equations 5a, 5b, 5c and 5d. In order to perform the equilibrium calculation, the model is required to solve the equations 6, 7, 8 and 9 for material balance and K-value.

The quantity of wax formed and the appearance point are determined at each flow temperature. The deposition of wax occurs in the present of any single or combination mechanisms as prescribed above. The rate of deposition is calculated by using a typical equation given below:

$$m = k(C_{\text{bulk}} - C_{\text{wall}}) \quad [1]$$

where: m = deposition rate
 k = mass transfer coefficient
 C = local concentration of wax formers in the liquid.

The local concentration of wax forming components in the bulk oil and at the wall is determined by using the developed thermodynamic model. Mass transfer coefficients from the liquid to the wall are determined

for each pipe segment depending on the local flowing conditions and fluid properties:

$$Sh = 0.015 \times Re^{0.88} Sc^{1/3} \quad [2]$$

Where : $Sc = (\mu_l \rho_l) / D$

Re = Reynolds Number

$$Sh = (k D_h) / D \quad [3]$$

Where

D = Diffusivity of wax in oil

D_h = Hydraulic radius

μ_l = Liquid viscosity

ρ_l = Liquid density

k = Mass transfer coefficient

CASE STUDY

Figure 1 shows the calculated results of the amount of wax precipitated for Perdana oil as a function of temperature at atmospheric pressure. Also the model could predict cloud point of the oil and the wax distribution in each component in the whole oil. It was reported that the crude contained 79 percent of normal paraffin component and 21.6 percent of wax content. The specific gravity and pour point were 0.8361 and 36°C respectively. The Perdana field is producing waxy crude oil and is expected to face problem of deposition along the production tubing, surface facilities and in the pipeline.

Model Verification

The wax equilibrium model was verified with experimental data obtained from Petronas Research and Scientific Services (PRSS). The cloud point of the Perdana oil was 39.2°C and the cloud point for the oil calculated by the model was 40.54°C. The model has shown an encouraging performance in predicting the cloud point with such high accuracy. The model also predicted the wax precipitation for each component based on weight percent of solid phase in the oil. The amount of insoluble wax as a function temperature is shown in Figure 1. The wax distribution analysis for each component for comparison is shown in Figure 2 for carbon number from C12 to C19. The quality of data from the experiment depends on the ability to separate oil from wax.

Discussion of Results

Figure 2 has shown that the calculated result predicted within the range of 3 weight percent of wax as compared to measurement data. Won's model had considered paraffin components only as wax constituents. Samples used in the laboratory analysis may be contained aromatics and impurities such resin, sand and clay particles that will act as nuclei for wax crystallization. Higher result from the measurement was due to the presence of these components in the deposited wax.

Since inadequate of measured data for higher carbon number, comparison for the whole wax composition incomplete. The model was incapable of representing all the details of an oil mixture. An oil mixture consists of thousands of different components. In the model of Won, it was assumed that the liquid and solid phase heat capacities were equal. But experimentally proved that the heat capacity difference was a linear function of temperature and proportional to the molecular weight. The calculated cloud point is used to determine the depth above which paraffin deposits in well as shown in Figure 3. This is a significant step that should be taken at the earlier stage in managing wax in an oil well. Most of the preventive and remedial techniques refer to the depth of cloud point as the deepest depth of deposition. The heat loss and temperature drops along the production tubing that contribute to the appearance of wax must be calculated separately. The calculation considers the thermal conductivity of fluids, rock and pipe. The heat loss from the hot oil to the surrounding is due to the convection and conduction effects.

The model did not consider the effect of pressure during the oil flow in pipe. It was also assumed that concentration of lighter components in oil remained unchanged. However, since the flow in the production tubing was categorized as slightly compressible, concentration of paraffin wax in oil adversely vary with the lighter components. Pressure decreases as oil flows from the bottom hole of well to the surface. Lighter components in oil are liberated as gases and concentration of heavier components such as paraffin wax increases. At the point where the thermodynamic equilibrium is achieved the paraffin wax will appear as a solid phase in oil.

CONCLUSIONS

Great potential savings can be derived from accurate prediction of wax formation in offshore systems at an early phase in the project. Knowledge of the magnitude of wax deposition can lead to reduction of insulation requirements for production and transportation systems. Conversely, problems with wax can be addressed at the early stage of a project so that sufficient thermal insulation could be planned for instead of expensive chemical injection and loss in capacity availability. The minimum pigging frequency can be determined if the amount of wax deposition can be estimated. In addition, problems related to start-up and shutdown can be solved in a more effective manner.

However, the mathematical model requires a very detailed oil analysis as input data. Detailed information about the hydrocarbon group type distribution (n-alkanes, isoalkanes, naphthenes, etc) of the heavy ends of the oils, and particularly those of the first part of wax crystallizing from the oils, are essential for the improvement of the model.

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EQUATIONS

$$F = S + L \quad (A)$$

where

F = Total number of moles in the feed
S, L = Total number of moles in the wax and oil phase

$$Z_F = X_S + X_L \quad (B)$$

where

Z, X_S, X_L = Feed, wax and oil phase mole fractions for i-th component

$$K_i = X_S / X_L \quad (C)$$

where

K = Equilibrium K-value of the i-th Component

$$K = \gamma_i^L / \gamma_i^S \exp [\Delta H_i^f / RT (1 - T / T_i^f)] \quad (D)$$

where

γ = Activity coefficient
T_f = Fusion temperature
 ΔH^f = Heat of fusion
T = Temperature
R = Gas constant
L = Liquid phase
S = Solid phase

$$\ln \gamma_i = V_i (\delta_i' - \delta_i)^2 / RT \quad (E)$$

$$\delta_i' = \sum \phi_i \delta_i \quad (F)$$

$$\phi_i^L = X_i^L V_i^L / \sum X_i^L V_i^L \quad (G)$$

$$\phi_i^S = X_i^S V_i^S / \sum X_i^S V_i^S \quad (H)$$

where

V = Molar volume
 δ = Solubility parameter
 ϕ = Component volume fraction
 δ_i' = Average solubility parameter of the mixture
L = liquid phase
S = Solid phase

$$\Delta H_i^f = 0.1426 MW_i T_i^f \quad (I)$$

$$T_i^f = 374.5 + 0.02617 MW_i - 20172 / MW_i \quad (J)$$

$$V_i = V_i^L = V_i^S = MW_i / d_i^L \quad (K)$$

$$d_i^L = 0.8155 + 0.6272 \cdot 10^{-4} MW_i - 13.06 / MW_i \quad (L)$$

where

MW_i = Molecular weight
d_i^L = Liquid phase density